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# Organic Microporous Nanofillers with Unique Alcohol Affinity for Superior Ethanol Recovery toward Sustainable Biofuels

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## Accepted Article

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**Authors:** Xi Quan Cheng, Kristina Konstas, Cara M. Doherty, Colin D. Wood, Xavier Mulet, Zongli Xie, Derrick Ng, Matthew R. Hill, Cher Hon Lau, and Lu Shao

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A Journal of



# Organic Microporous Nanofillers with Unique Alcohol Affinity for Superior Ethanol Recovery toward Sustainable Biofuels

Xi Quan Cheng <sup>[a,b,f]</sup>, Kristina Konstas <sup>[b]</sup>, Cara M. Doherty <sup>[b]</sup>, Colin D. Wood <sup>[c]</sup>, Xavier Mulet <sup>[b]</sup>, Zongli Xie <sup>[b]</sup>, Derrick Ng <sup>[b]</sup>, Matthew R. Hill <sup>[b,d]</sup>, \* Cher Hon Lau <sup>[b,e]</sup>, \* and Lu Shao <sup>[a]</sup>, \*

**Abstract:** To minimize energy consumption and carbon footprints, pervaporation membranes are fast becoming the preferred technology for alcohol recovery. However this approach is only confined to small-scale operations as the flux of standard rubbery polymer membranes remain insufficient to process large solvent volumes, while membrane separation using glassy polymer membranes are prone to physical aging. This study reports the alcohol affinity and intrinsic porosity of networked, organic, microporous polymers can simultaneously reduce physical aging, drastically enhance both flux and selectivity of a super glassy polymer, poly-[1-(trimethylsilyl)-propyne] (PTMSP). Slight loss in alcohol transportation channels in PTMSP is compensated by the alcohol affinity of the microporous polymers. Even after continuous exposure to aqueous solutions of alcohols, PTMSP pervaporation membranes loaded with the microporous polymers outperform to state-of-the-art and commercial pervaporation membranes.

Ethanol (EtOH) is a valuable commodity for the transportation industry, as it reduces harmful emissions that contribute to global warming.<sup>[1]</sup> It is also a common raw material in the food and pharmaceutical industries. EtOH is generally produced through yeast fermentation of sugar, or starch-containing materials. Fermentation is a slow process and stops when the EtOH concentration reaches about 13 %. To ensure yeast survival whilst maximizing fermentation efficiency, EtOH must be removed and recovered from the reaction mixture. Traditional EtOH recovery processes such as multi-stage distillation, azeotropic distillation, and molecular sieving have large carbon footprints for solvent vaporization and sieve regeneration. Meanwhile the use of entrainers in azeotropic

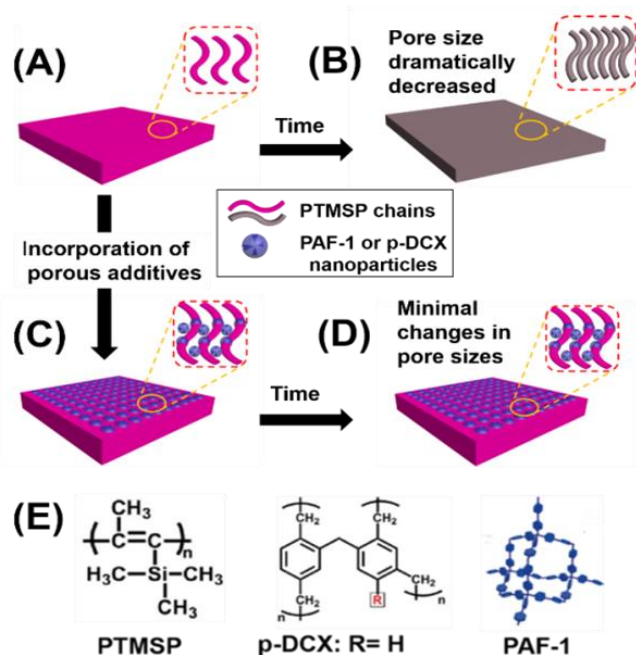
distillation poses safety concerns during operations.<sup>[2]</sup> Alternatively, EtOH can be purified using a hybrid process of pervaporation and distillation;<sup>[3]</sup> offering integration with the fermentation step.<sup>[4]</sup> This potentially improves fermentation efficiencies and yields, whilst transforming process efficiencies.

Pervaporation occurs where liquid solvents permeate through a non-porous membrane, followed by downstream solvent evaporation under vacuum.<sup>[5]</sup> Advantages of pervaporation over other separation techniques include low carbon footprints, minimal spatial requirements, and the lack of moving parts.<sup>[6]</sup> To fully maximize the economic advantages of a hybrid process, an ideal pervaporation membrane should have a flux of 0.15 kg m<sup>-2</sup> h<sup>-1</sup> and a EtOH/water selectivity of 10.3.<sup>[3]</sup> Ascribing to high EtOH/water selectivity, and stable fluxes,<sup>[6]</sup> hydrophobic rubbery polymers such as polydimethylsiloxane (PDMS) have been deployed to maximize the potential of pervaporation in hybrid processes during EtOH recovery.<sup>[7]</sup> The cost and carbon footprint of fermentation-pervaporation hybrid processes can be further minimized by enhancing the solvent flux and selectivity of pervaporation membranes.

The solvent flux of PTMSP is twice as fast as current-state-of-the-art PDMS-based membranes,<sup>[8]</sup> and similar EtOH/water selectivity. Unfortunately, the initial ultrapermeances of PTMSP are not retained, due to rapid physical aging;<sup>[9]</sup> circumventing their real-world applications. Polymer physical aging is a natural phenomenon as polymer chains tend to converge towards a thermodynamic equilibrium;<sup>[10]</sup> collapsing pockets of free space between polymer chains i.e. fractional free volume (FFV) content.<sup>[11]</sup> Through batch gas permeation experiments, we previously reported that physical aging in PTMSP can be overcome with porous, organic polymeric fillers like the archetypal porous aromatic framework, PAF-1,<sup>[12]</sup> and hypercrosslinked polymers (HCPs).<sup>[13]</sup>

Porous aromatic framework (PAF-1) is made up of aromatic rings linked together in a tetrahedron,<sup>[14]</sup> while a polydichloroxylene (p-DCX) hypercrosslinked polymer comprises xylene units linked together through methylene bridging (**Figure 1**).<sup>[15]</sup> Both polymers have aromatic rings that may facilitate intimate non-bonding interactions with PTMSP chains. Such interactions immobilize PTMSP chains and prevent the collapse of fractional free volume (FFV) content that abates physical aging in super glassy polymers.<sup>[12-13, 16]</sup> Akin to other nanofillers, the blending of these porous, organic polymers only enhanced PTMSP flux, leaving the selectivity of molecules intact. Even the presence of functional groups with high affinity towards targeted molecular species on nanofillers did not enhance molecular selectivity.<sup>[16a]</sup> Moreover the anti-aging capabilities of such polymer blends have not been characterized during continuous long term operation, particularly for pervaporation.

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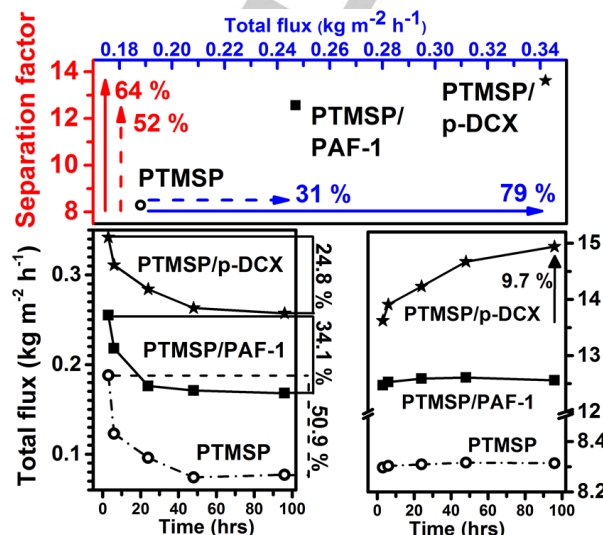


**Figure 1.** (A) PTMSP membranes undergo (B) physical aging and lose their pervaporation performances over time. (C)&(D) The incorporation of PAF-1 and p-DCX additives into PTMSP can mitigate the effects of physical aging through their organophilicity. (E) Chemical structures of PTMSP, p-DCX, and PAF-1 polymers.

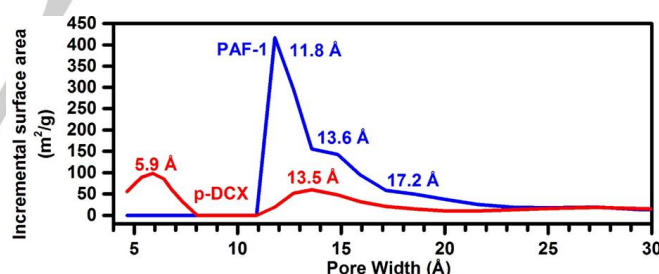
Here we report that 10 wt. % of PAF-1 or p-DCX can simultaneously enhance both total flux and EtOH/water selectivity, whilst overcoming physical aging in 100  $\mu\text{m}$  thick unsupported PTMSP pervaporation membranes. Pervaporation experiments were performed at 40  $^{\circ}\text{C}$ , with upstream and downstream pressures of 760 and 5 Torr, over 96 hours of continuous operation. The PTMSP used in this work is commercially available from Gelest Inc., while PAF-1 and p-DCX are synthesized according to literature.<sup>[14,15]</sup> Complimentary characterisation techniques such as bulk positron annihilation lifetime spectroscopy (PALS) and alcohol adsorption revealed that the sorption capabilities of both PAF-1 and p-DCX polymers are key to yielding anti-aging pervaporation membranes.

**Figure 2** shows that the total flux of PTMSP membranes was increased by 31 % and 79 % with 10 wt. % PAF-1 and p-DCX, respectively; while solution NMR experiments revealed that the EtOH/water selectivity increased by 52 % (PAF-1) and 65 % (p-DCX). The simultaneous enhancements in total flux and EtOH/water selectivities of both PTMSP/PAF-1 and PTMSP/p-DCX membranes are atypical of most other PTMSP/additive membranes<sup>[17]</sup> that display a trade-off relationship between total flux and selectivity. This flux-selectivity trade-off is similar to that described by Robeson's plots for gas separation membranes,<sup>[18]</sup> where increments in total flux are reflected by a decrease in molecular selectivity, and vice versa. The pores of hydrophobic PAF-1 and p-DCX polymers could provide additional channels for molecular transport (**Figure 3**), thus improving the total flux of our PTMSP/additive membranes. Meanwhile the exceptional surface areas of these hydrophobic additives provide more adsorption sites that favored alcohol adsorption over water;<sup>[19]</sup>

thus improving the EtOH/water selectivity. The combination of enhanced molecular adsorption and additional porosity for molecular diffusion accounted for drastic enhancements in both total flux and EtOH/water selectivity. More importantly, PAF-1 and p-DCX also inhibited physical aging in PTMSP pervaporation membranes.



**Figure 2.** The effects of PAF-1 and p-DCX on the pervaporation performances of 100  $\mu\text{m}$  thick PTMSP membranes. Pervaporation experiments were conducted for 96 hours with mixtures comprising 10 wt. % EtOH in water. The upstream pressure was kept at 760 Torr, while the downstream pressure was maintained at 5 Torr. The operating temperature was maintained at 40  $^{\circ}\text{C}$ . The EtOH/water selectivities of these membranes were determined using solution state NMR. Each data point of the separation performance is an average of three repetitions of each test, with  $\pm 5$  % standard deviation.

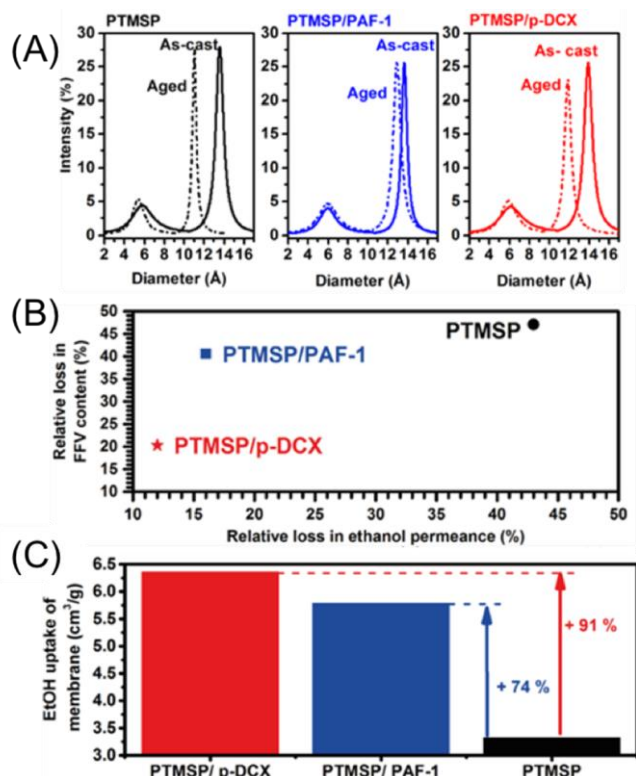


**Figure 3.** The surface area contributed by different pore size distributions of PAF-1 (blue) and p-DCX additives used in this work.

Like other PTMSP that were synthesized over judiciously chosen catalytic systems,<sup>[4]</sup> pervaporation membranes fabricated from commercially available PTMSP studied here lost 51 % of the total flux in nearly 100 hours of continuous operation. Meanwhile PAF-1 and p-DCX only reduced the total flux of these membranes by 34 % and 25 %, respectively. The EtOH/water selectivity of aged PTMSP/p-DCX membranes increased by 10 % while the selectivities of aged PTMSP and PTMSP/PAF-1 membranes remained the same. Compared to gas separation membranes, the ability of PAF-1 and p-DCX to inhibit physical aging in PTMSP is less pronounced during pervaporation. This is attributed to the different sizes of targeted molecules. The kinetic diameter of EtOH molecules is 4.5  $\text{\AA}$ ,<sup>[20]</sup> while gas



molecules are smaller than 3.8 Å. The impact of physical aging on FFV content in membranes studied here is tracked by PALS.



**Figure 4** (A) PALS analysis of as-cast (solid) and aged (dashed) PTMSP (black), PTMSP/PAF-1 (blue), and PTMSP/p-DCX (red) membranes. (B) Relative losses of total flux as a function of loss in FFV content across PTMSP, PTMSP/PAF-1, and PTMSP/p-DCX membranes. (C) Solvent uptake of membranes studied here in this work.

Bulk PALS experiments were conducted at ambient conditions. Physical aging reduced the concentration and pore sizes in PTMSP (**Figure 4**). The larger pore size distribution centered at 14 Å was reduced to 11 Å; accounting for the 50 % reduction in total flux. Both PAF-1 and p-DCX additives mitigated pore shrinkage leading to lower flux loss. Systems comprising non-compatible additives<sup>[21]</sup> can yield nanogaps (as wide as 8 Å) between additives and polymer chains<sup>[22]</sup> that reduce EtOH/water selectivity<sup>[23]</sup> by allowing both water (2.8 Å)<sup>[24]</sup> and EtOH (4.5 Å)<sup>[20]</sup> molecules to permeate across membranes. However, from PALS analysis, it was clear that such nanogaps were absent in PTMSP/PAF-1 and PTMSP/p-DCX films studied here. The absence of nanogaps in PTMSP/PAF-1 membranes accounted for the unchanged EtOH/water selectivity over time. The unchanged EtOH/water selectivity in aged PTMSP/PAF-1 membranes implied that the permeation of EtOH and water across these membranes were uniformly reduced by physical aging. Interestingly, the EtOH/water selectivity of aged PTMSP/p-DCX membranes increased by nearly 10 %. The total flux of aged PTMSP/p-DCX membranes remained higher than any membranes studied here and elsewhere, because of higher solvent solubility coefficients. **Figure 4B** shows that p-DCX loaded samples lose twice as much FFV content when compared to PAF-1-based membranes.

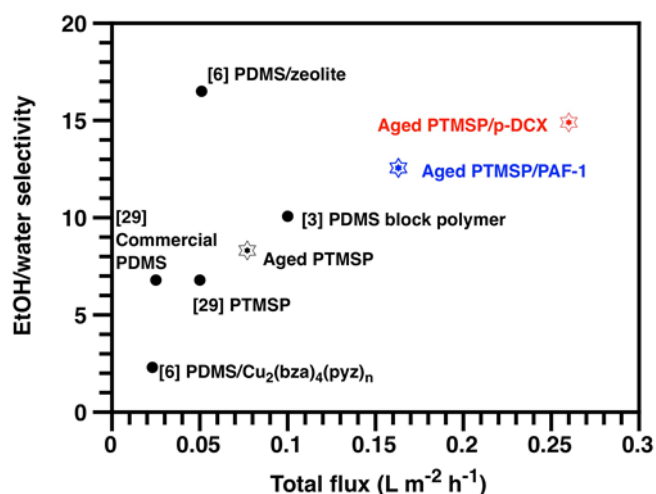
Clearly solvent sorption is more dominant than molecular diffusion via FFV content during molecular transport in pervaporation. The incorporation of p-DCX and PAF-1 additives enhanced EtOH sorption in resulting PTMSP membranes by 74 % and 91 %, respectively. This was attributed to solvent swelling the PTMSP matrix and p-DCX additives.<sup>[25]</sup>

As EtOH concentration increased from 3 to 10 wt. % in water, the total flux of PTMSP/p-DCX membranes increased from 0.13 to 0.22 kg m<sup>-2</sup> h<sup>-1</sup>, a 70 % increment (**Figure S2**). However the EtOH/water selectivity of these membranes decreased by 16 %; indicating that more water was passing through the membrane. Higher EtOH concentrations can swell PTMSP polymer chains, enhancing water transport; resulting in lower EtOH/water selectivity.<sup>[26]</sup> As feed temperature increased from 20 to 60 °C, the total flux increased by ~ 113 % while EtOH/water selectivity decreased by 8 %. Higher temperatures increased vapour pressures on the feed side while the pressure at the permeate side is maintained; leading to larger driving forces across the membrane that enhanced the total solvent flux.<sup>[27]</sup> Higher temperatures can also provide sufficient energy to mobilize polymer chains, reducing EtOH/water selectivity. This is typically observed in systems where solvent adsorption is the dominant factor for solvent transport in membranes.<sup>[28]</sup>

To demonstrate the industrial viability of our membranes, we also performed PV experiments at 40 °C with a 15 Torr vacuum on the permeate side of a 5 µm thin PTMSP/PAF-1 membrane supported on polyvinylidene fluoride porous substrates (**Figure S3**). The initial total flux of this thin film membrane reached 1.6 kg m<sup>-2</sup> h<sup>-1</sup>—an 8-fold enhancement compared to thick film membranes, and an EtOH/water selectivity of 9. The drastic flux enhancement was attributed to the lower transmembrane resistance in thinner membranes. After 50 hours of continuous operation, the total flux decreased and stabilized to 0.7 kg m<sup>-2</sup> h<sup>-1</sup>, while EtOH/water selectivity decreased to 6. The lower solvent flux was attributed to the loss of FFV content in thinner membranes.<sup>[29]</sup> Polymer chain convergence during aging can combine free spaces together, leading to lesser FFV content but larger free spaces. This results in a decline of EtOH/water selectivity. Henceforth, the high total solvent fluxes of our PTMSP/PAF-1 and PTMSP/p-DCX membranes preclude the need to fabricate thin membranes that age rapidly.

The total flux of our aged PTMSP/PAF-1 and PTMSP/p-DCX membranes remained more superior to as-cast pristine PTMSP, polydimethylsiloxane (PDMS) mixed matrix membranes,<sup>[6]</sup> commercial pervaporation membranes,<sup>[30]</sup> and current-state-of-the-art PDMS membranes<sup>[8]</sup> (**Figure 5**). A major advantage of PTMSP-based PV membranes is the distinctively high flux and separation factors, which are threefold and twofold higher than PDMS.<sup>[30]</sup> PDMS, a semi-crystalline material that does not age physically, possess separation performance stability at the expense of high flux. The main concern of deteriorating solvent flux to extremely low values, especially in thin PTMSP membranes is resolved through the immobilization of PTMSP chains with additives showing high affinity towards alcohols. Due to the organic microporous nanofillers enhanced the permeable properties and inhibited the physical aging of

PTMSP, the composite materials may also show promise in application in gas separation,<sup>[12,16]</sup> organic solvent nanofiltration and many other fields.<sup>[31]</sup>



**Figure 5** Comparison of PTMSP/additive membranes studied here with state-of-the-art and commercial PDMS membranes. The pervaporation performances of our aged membranes surpass those of PDMS membranes.

**In conclusion**, by enhancing solvent sorption through the organophilicity of PAF-1 and hypercrosslinked polymers, and abating losses in free spaces, physical aging in PTMSP pervaporation membranes can be abated. Performance stability issues typically associated with collapsing free volume content in thin PTMSP membranes is addressed by mitigating the negative impact of collapsing free volume content. The high total solvent flux of PTMSP/PAF-1 and PTMSP/p-DCX membranes preclude the requirement of thin membranes that could contain defects to obtain high flux membranes. More importantly, these membranes can be fabricated using a facile approach, and commercially available materials. Therefore, the organic microporous nanofillers incorporated PTMSP PV membranes show strong promise in concentrating EtOH from the fermentation solutions.

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**Keywords:** Hypercrosslinked polymers, porous aromatic framework, pervaporation, polymer membranes

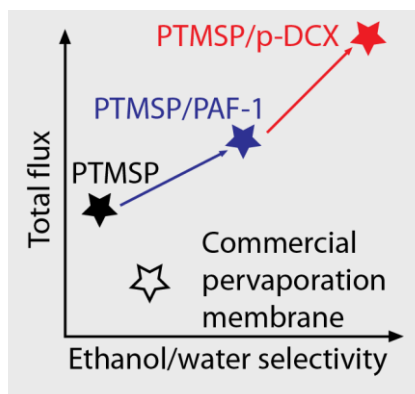
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## Entry for the Table of Contents

## COMMUNICATION

The organophilicity of networked, microporous polymers compensates the abated loss of molecular transportation pathways in aged super glassy polymer pervaporation membranes. This solves the issues of insufficient flux, physical aging whilst enhancing selectivity to yield superior pervaporation polymer membranes that can transform biofuel production.



*Xi Quan Cheng, Kristina Konstas, Cara M. Doherty, Colin D. Wood, Xavier Mulet, Zongli Xie, Derrick Ng, Matthew R. Hill, Cher Hon Lau, and Lu Shao*

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